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Dielectric relaxation of some diol / alcohol mixtures in different solvents

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Abstract : The static permittivity and dielectric loss in the frequency range 0.1-18 GHz at 20°C for four ternary mixtures of diol / diol / alcohol in three nonpolar solvents namely heptane, cyclohexane and mesitylene have been studied. The systems used are 1, 6 hexanediol + 1, 2 ethanediol + *n*-hexanol (HEH), 1, 6 hexanediol + 1, 2 ethanediol + cyclohexanol (HEC), 1, 12 dodecanediol + 1, 2 ethanediol + *n*-hexanol (DEH) and 1, 12 dodecanediol + 1, 2 ethanediol + cyclohexanol (DEC). The relaxation spectra have been analysed in three Debye terms. The lower frequency term characterized by τ_1 is predominating and is related to the association process. The dielectric behaviour in the different solvents is discussed.

Keywords . Dielectric spectroscopy, hydrogen bonding, ternary mixtures

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1. Introduction

The structure and dynamics of hydrogen-bonded liquids can be studied by dielectric relaxation spectroscopy. Alcohols as a large class of associating liquids have been extensively studied by dielectric spectroscopy regarding only pure liquids as well as their mixtures with nonpolar solvents[1-5]. Recently, association in mixtures like water or diol / mono-alcohol have been reported[6-7]. Further informations on the association in diol / alcohol mixtures could be gained by the study of dielectric behaviour of binary mixtures of diol / n-alcohol on dilution with a nonpolar solvent. From our laboratory the first results on the dielectric properties of a diol or a mixture of two diols in a monohydric alcohol diluted with a non-polar solvent (heptane) have been reported[8-10].

The aim of this work is to study the effect of two non-polar solvents, of structure different from that of heptane (namely mesitylene and cyclohexane), on the dielectric properties of some quaternary systems : diol / diol / *n*-hexanol / solvent. The effect of using cyclohexanol instead of *n*-hexanol on the dielectric behaviour of these systems will also be studied.

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2. Experimental

The dielectric loss ε'' for the investigated solutions at frequencies between 0.2-18 GHz was measured using a microwave swept frequency transmission spectrometer[11]. The description and calibration of a similar spectrometer have been given before[12]. The ε'' values are uncertain to about ± 4%.

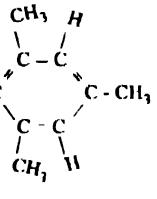
The static permittivity ε_S was measured at 2MHz using a WTW dipolemeter with an uncertainty of better than ± 2%. The refractive index n_D was measured by an Abbe refractometer to an uncertainty of ± 1.10^{-4}. Chemicals from Fluka, Merck, B.D.H and Aldrich (purity > 98 – 99%) were used as obtained.

Measurements of ε_S and ε'' were carried out at 20°C. Using a four letter abbreviation, DEAS where D denotes the first diol, E the second diol 'ethanediol' which is common in all mixtures, A the monohydric alcohol and S the non-polar solvent, the following systems are investigated :

1. 1, 6 Hexanediol + 1, 2 Ethanediol + *n*-Hexanol in Cyclohexane (HEHC)
   1, 6 Hexanediol + 1, 2 Ethanediol + *n*-Hexanol in Mesitylene (HEHM)
   1, 6 Hexanediol + 1, 2 Ethanediol + *n*-Hexanol in Heptane (HEHH)*
2. 1, 6 Hexanediol + 1, 2 Ethanediol + Cyclohexanol in Cyclohexane (HECC)
   1, 6 Hexanediol + 1, 2 Ethanediol + Cyclohexanol in Mesitylene (HECM)
   1, 6 Hexanediol + 1, 2 Ethanediol + Cyclohexanol in Heptane (HECH)
3. 1, 12 Dodecanediol + 1, 2 Ethanediol + *n*-Hexanol in Cyclohexane (DEHC)
   1, 12 Dodecanediol + 1, 2 Ethanediol + *n*-Hexanol in Mesitylene (DEHM)
   1, 12 Dodecanediol + 1, 2 Ethanediol + *n*-Hexanol in Heptane (DEHH)*
4. 1, 12 Dodecanediol + 1, 2 Ethanediol + Cyclohexanol in Cyclohexane (DECC)
   1, 12 Dodecanediol + 1, 2 Ethanediol + *n*-Hexanol in Mesitylene (DECM)
   1, 12 Dodecanediol + 1, 2 Ethanediol + *n*-Hexanol in Heptane (DECH)

In the mentioned systems, the diols and alcohols are the solutes, while heptane, cyclohexane and mesitylene are the non-polar solvents used. Heptane and cyclohexane are aliphatic solvents. They are of different shapes. Heptane is a straight chain compound of formula : $CH_3(CH_2)_5CH_3$. Cyclohexane is a ring or closed chain compound composed of six saturated carbon atoms of formula : $CH_2(CH_2)_4CH_2$ On the other hand, the third solvent, mesitylene, or 1, 3, 5-trimethylbenzene, is an aromatic hydrocarbon of formula : $(CH_3)_3C_6H_3$ of

structure



The molar ratio 1 : 4 for the first diol to ethanediol is kept the same for all systems. Also,

* data for HEHH and DEHH were taken from reference [13]

the molar ratio of the diols in the aliphatic alcohols 1 : 9 is kept the same. Concentrations of the alcoholic mixtures in the non-polar solvents ranging from 0.08 to 0.3 mole fraction only were used as higher concentrations could not be measured by the available apparatus.

3. Results and Discussion

Static permittivity :

The static permittivity ε_S and refractive index n_D for the investigated systems were measured at 20°C. The values of the normalized dispersion step $S/x = (\Delta\varepsilon_S - \Delta n_D^2)/x$ were calculated and are given in Table 1. $\Delta\varepsilon_S$ and Δn_D^2 are the differences in the static permittivities and refractive indices square of the solution and solvent and x is the total alcoholic concentration in mole fraction in the different non-polar solvents.

Table 1. Normalized dispersion step s/x for the investigated quaternary **diol/diol/alcohol/solvent** systems at 20°C. x is the total alcoholic concentration in mol%

n-Hexanol systems (xEHx)

x [mol%]	s/x	x [mol%]	s/x	x [mol%]	s/x
HEHH		**HEHM**		**HEHC**	
8	1.53	12	2.60	12	2.45
14	1.75	15	2.66	15	2.63
20	2.15	20	2.89	20	2.95
25	2.41	25	3.15	25	3.38
30	2.75	30	3.44	30	3.88
DEHH		**DEHM**		**DEHC**	
12	1.72	10	2.46	10	2.24
15	1.83	15	2.62	15	2.49
20	2.08	20	2.80	20	2.81
25	2.38	25	3.05	25	3.22
30	2.66	30	3.34	30	3.68

Cyclohexanol systems (xECx)

x [mol%]	s/x	x [mol%]	s/x	x [mol%]	s/x
HECH		**HECM**		**HECC**	
8	1.95	8	2.65	10	2.57
14	2.37	14	2.84	15	2.89
20	2.77	20	3.12	20	3.29
25	3.11	25	3.35	25	3.85
30	3.43	30	3.67	30	4.52
DECH		**DECM**		**DECC**	
12	2.16	12	2.60	10	2.83
15	2.32	15	2.79	15	3.11
20	2.63	20	3.13	20	3.53
25	2.78	25	3.37	25	3.99
30	3.13	30	3.76	30	4.50

The measured values of S/x for the investigated systems at 20°C are illustrated versus x in Figure 1. It is clear that the mixtures diluted with heptane have the lowest values of S/x while those using cyclohexane are higher than them. In the case of mesitylene solutions, S/x values are higher than those for heptane solutions for all concentrations. For cyclohexane solutions, only for high concentrations (x > 15 mol %) S/x is higher than that for mesitylene solutions, with the exception of the DECC system where S/x values are higher than the DECM values for all concentrations.

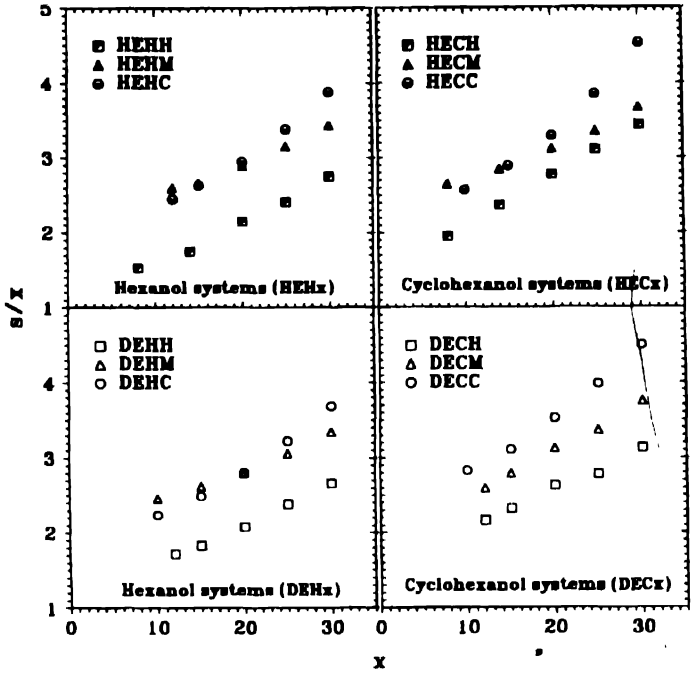


Figure 1. Normalized dispersion step S/x *versus* concentration x, 20°C. x (mole fraction) is the concentration of the total alcoholic mixture in the different solvents.

Relaxation spectra :

The specific dielectric loss $\Delta\varepsilon''/x$ was measured for the same systems at frequencies (f) between 0.2 and 16 GHz and at 20°C. Δ here means the difference in dielectric loss between the investigated solutions and solvents used. The data obtained are illustrated graphically in Figure 2. All spectra are broader than a Debye curve, as commonly found with alcoholic systems which suggests a distribution of relaxation times. So, we tried to fit the experimental data by the sum of two Debye terms using the equation :

$$\Delta\varepsilon''/(\Delta\varepsilon_S - \Delta n_D^2) = \sum G_i \frac{\omega\tau_i}{1+\omega^2\tau_i^2}$$

where G_i is the relaxation strength of each term and $\Sigma G_i = 1$. The fit quality is improved by employing an additional Debye-type spectral component on the high frequency side. Anyhow, due to the restricted experimental frequency range (0.2–16 GHz), we could not fit the data by more than three Debye components (characterized by τ_1, τ_2 and τ_3). Results for systems HEHC

and HECC, chosen as a representative selection, are illustrated in Figure 3. This figure shows that τ_1 and τ_2 could be accurately determined from the experimental data. τ_3 is less accurate as

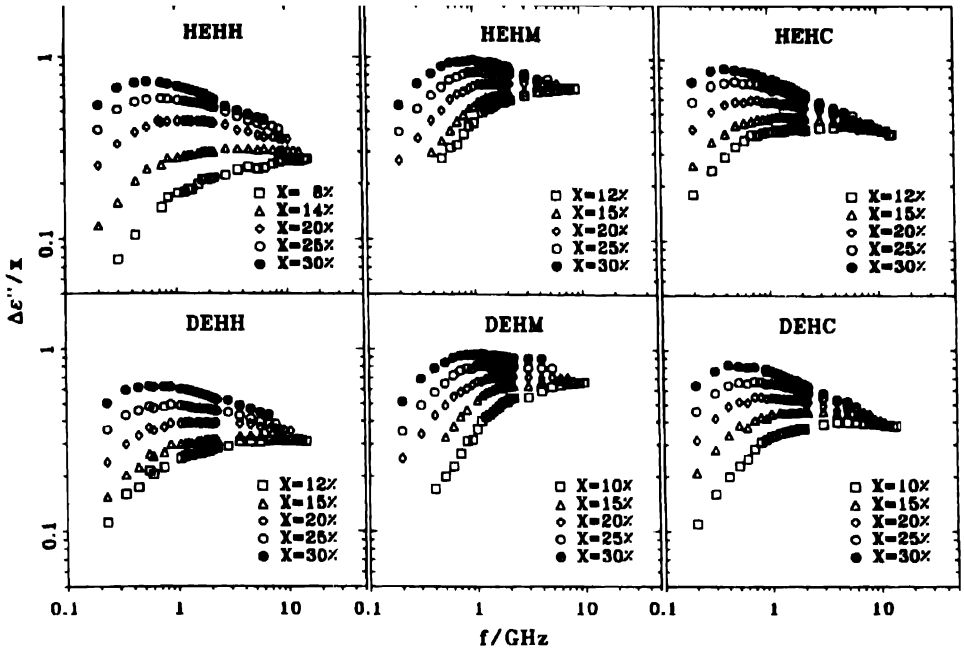


Figure 2(a). Specific dielectric loss ($\Delta\varepsilon''/x$) *versus* frequency (f) for n-hexanol systems for different concentrations x and 20°C

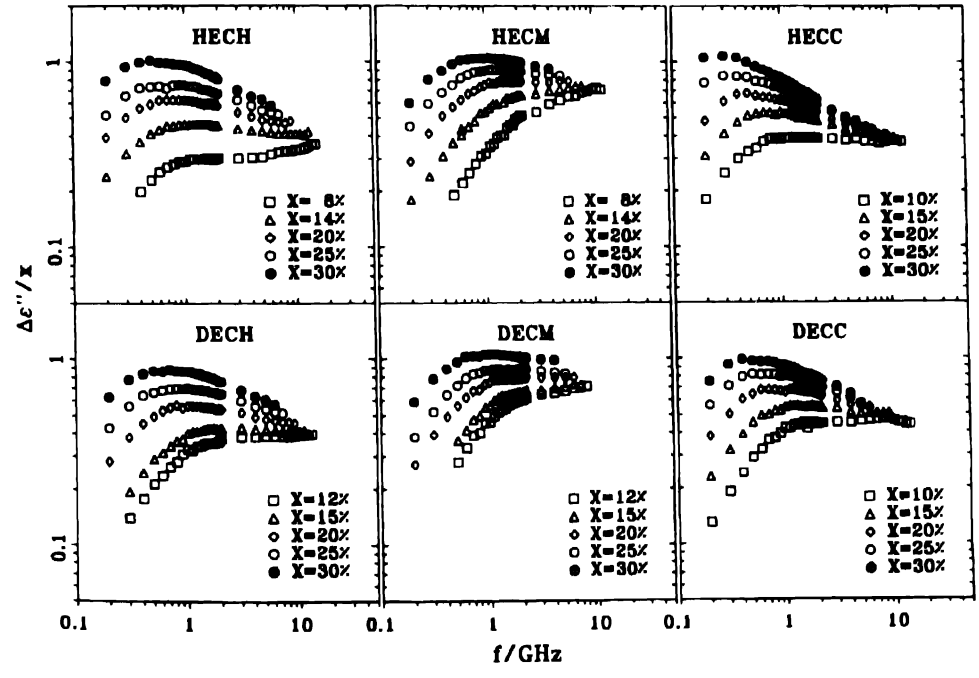


Figure 2(b). Same as in Figure 2(a) Cyclohexanol is used instead of n-hexanol

the maximum of this absorption term lies outside the experimental data and it is found to be around 10ps. Such a value was found before[11-13] and so it is kept constant throughout the

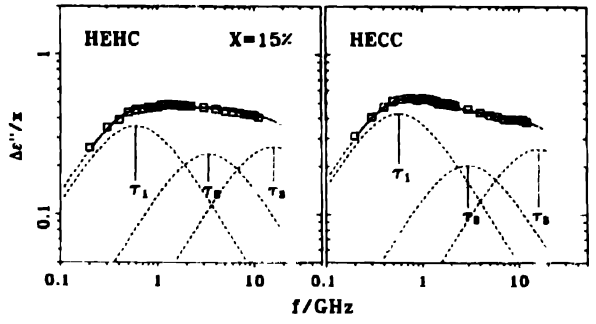


Figure 3. Absorption curves for the systems HEHC and HECC, 20°C. Fitting the experimental ($\Delta\varepsilon''/x$) values using 3 Debye terms (solid line)

analyses. The values of τ_1, τ_2, τ_3 and the normalized relaxation strengths ($G_i = S_i/S$) for τ_1 and τ_2 are given in Table 2. In this table, the values of G_3 are not given as the accuracy in them is less than that in G_1 and G_2 and we contented ourselves with the values of $[1 - \Sigma G_i]$ and its variation with concentration as it gives an insight about the dipolar absorption in the millimeter and FIR regions. Fitting of the data was done by a computer program. The results are uncertain to about 5%.

We are mainly interested in the principal absorption term for the investigated systems in the different solvents. τ_1 values are illustrated in Figure 4 *versus* concentration in mol %. It

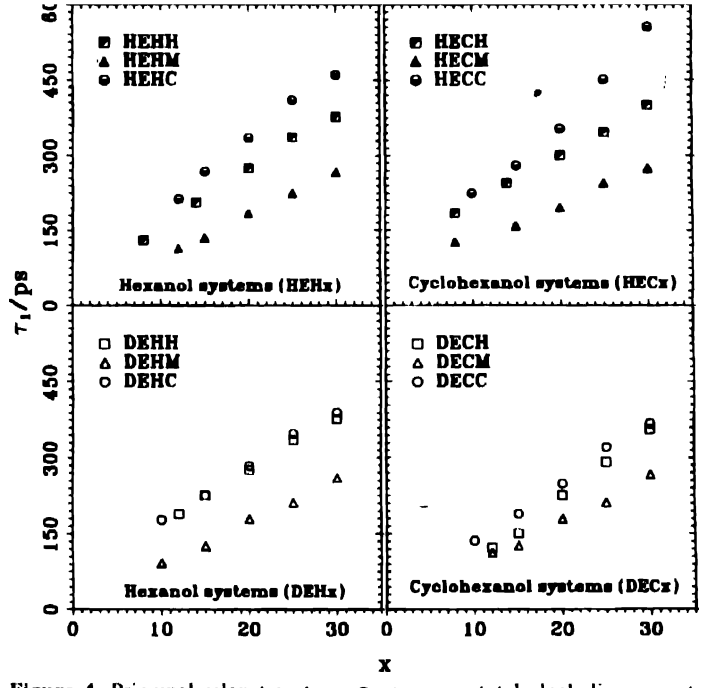


Figure 4. Principal relaxation time τ_1 ps *versus* total alcoholic concentration x for the investigated systems in the different solvents.

Table 2. Relaxation times τ_i (i = 1–3) and normalized relaxation strengths G_i for the investigated quaternary **diol/diol/alcohol/solvent** systems. 20°C. x is the total alcoholic concentration in mol% and η the viscosity.

n-Hexanol systems (xEHx)

x [mol%]	τ_1 [ps]	τ_2 [ps]	τ_3 [ps]	G_1	G_2	$1-\sum_{i=1}^{2} G_i$
HEHH						
8	130	40	10	0 15	0 12	0 74
14	206	48	10	0 21	0 16	0 63
20	275	63	10	0 29	0 19	0 52
25	336	69	10	0 38	0 21	0 41
30	377	75	10	0 43	0 21	0 36
HEHM						
12	113	37	10	0 21	0 21	0 58
15	134	39	10	0 27	0 21	0 52
20	184	42	10	0 33	0 22	0 45
25	225	46	10	0 38	0 21	0 40
30	267	62	10	0 43	0 23	0 34
HEHC						
12	213	40	10	0 23	0 17	0 60
15	268	48	10	0 27	0 18	0.55
20	335	63	10	0.32	0 19	0 49
25	410	71	10	0 37	0 18	0 45
30	460	83	10	0 40	0.16	0.44
DEHH						
12	189	40	10	0 19	0 16	0 64
15	225	41	10	0 22	0 19	0 60
20	275	49	10	0 26	0 21	0 53
25	336	62	10	0 30	0.22	0 48
30	377	71	10	0.37	0.23	0 41
DEHM						
10	120	40	10	0 18	0 17	0 65
15	126	40	10	0.25	0.21	0 54
20	179	40	10	0 33	0 22	0 45
25	212	40	10	0 38	0.24	0.38
30	260	40	10	0 44	0.27	0 28
DEHC						
10	177	40	10	0 17	0 18	0.64
15	225	43	10	0 26	0 19	0 55
20	284	50	10	0 30	0 18	0 52
25	348	60	10	0 33	0.19	0.48
30	390	69	10	0 37	0.18	0 45

Table 2. *(Cont'd.)*

Cyclohexanol systems (xECx)

x [mol%]	τ_1 [ps]	τ_2 [ps]	τ_3 [ps]	G_1	G_2	$1-\sum_{i=1}^{2} G_i$
HECH						
8	184	40	10	0.22	0.12	0 66
14	245	50	10	0 29	0.15	0 55
20	300	62	10	0 34	0 19	0.47
25	346	69	10	0 38	0 22	0 40
30	400	80	10	0 48	0.24	0 27
HECM						
8	126	39	10	0 10	0.22	0.69
14	159	40	10	0 22	0 24	0.55
20	195	44	10	0 31	0.24	0 45
25	245	49	10	0.38	0.25	0.37
30	275	55	10	0 44	0 25	0 31
HECC						
10	224	43	10	0.23	0 12	0.65
15	280	54	10	0 30	0 14	0 56
20	353	62	10	0 36	0 13	0 51
25	450	71	10	0 40	0 13	0 47
30	555	82	10	0 43	0 13	0 44
DECH						
12	123	33	10	0.23	0 12	0 65
15	150	36	10	0 25	0 15	0 59
20	225	44	10	0.35	0 17	0.48
25	291	56	10	0 39	0 23	0 37
30	356	63	10	0.46	0 25	0 28
DECM						
12	113	42	10	0 22	0.18	0 60
15	126	42	10	0 27	0 19	0 55
20	179	42	10	0.33	0 23	0.45
25	212	42	10	0 37	0 24	0.39
30	267	42	10	0 44	0.28	0 28
DECC						
10	136	33	10	0.23	0 11	0.67
15	189	36	10	0.28	0.14	0 58
20	248	46	10	0.32	0.14	0.53
25	321	56	10	0.34	0.17	0 49
30	368	66	10	0 38	0.16	0.46

is clear from this figure that τ_1 increases with increasing concentration. τ_1 values are different in the different solvents used. The lowest values of τ_1 are found in the systems using the aromatic solvent mesitylene although the viscosity of mesitylene (η = 0.85 mPa. s) is much higher than that of heptane (η = 0.41 mPa. s). This could be due to the solute-solvent interactions which are influenced by the nature of the solvent. In mesitylene, the solute-solvent interactions are much higher than that in heptane due to interaction between H-atom of an OH-group and π electrons in the aromatic ring of mesitylene molecule. This interacting environment around solute molecules leads to shorter life time τ_1 of the formed complexes. This behaviour was noticed before in benzene by Swain and Roy[14]. He stated also that "the interacting environment around solute species gives favourable alignment of dipoles of solute species resulting in high dipole moments *i.e.* high S/x". Figure 1 shows that S/x for systems using mesitylene are higher than those using heptane where the interaction of solute molecules in *n*-heptane environment is least. This is in favour of our interpretation for the behaviour of mesitylene systems. For cyclohexane solutions, τ_1 is higher than that for heptane solutions (Figure 4), this behaviour could be due to the cyclic shape of the cyclohexane molecule which will make the interaction of the solute molecules in cyclohexane enviroment lower than in mesitylene and heptane leading to longer life time τ_1 of complexes.

For the assignment of relaxation processes to the different terms obtained from the analysis, the first term characterized by τ_1 is surely related to the association process, we cannot exclude the existence of long-lived, well defined clustered objects. τ_1 reflects the life time of these clusters. The relaxation strength G_1 is dependent on concentration and increases with increase in concentration as expected. The second absorption region characterized by τ_2 is related to orientation of fragmental parts of these large clusters in the case of the solvent heptane as the relaxation strength G_2 in this case increases with increase in concentration. While in the case of the solvents mesitylene and cyclohexane G_2 is found to be the same in each solvent for all systems. In this case τ_2 could describe the switch over process from one hydrogen bond to another within the cluster. The term with short relaxation time τ_3 may be related to segmental motion in single molecules. Its relaxation strength is included in the term $1 - \Sigma G_i$ and the rest of this term may be related to polar group rotation or liberational motion.

To sum up, the change of solvent alters the dielectric behaviour of the different systems. The solute-solvent interaction in mesitylene is found to be much higher than in heptane and cyclohexane. The change from *n*-hexanol to cyclohexanol causes some disturbances in the medium due to its cyclic shape.

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